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THE DETERMINATION OF OXYGEN CONSUMED

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(W. Allan Moore)

Numerous attempts have been made in the past 75 years to devise a chemical method for the estimation of the strength of waste products of either human or industrial origin. Impetus has been given to this problem due to the fact that an answer could be obtained in a much shorter time than with the standard biological method. However, because of the complexity of various samples of wastes the metabolic activities of the flora and fauna present do not necessarily follow a constant rate. For this reason, it is apparent that any chemical method proposed could not correlate with the biochemical determination of oxygen demand.

However, it is often desirable to know in a minimum time the approximate oxygen absorbing power of a waste sample. A chemical oxygen consumed method is most satisfactory for this purpose.

In the case of some industrial wastes toxic materials may be present that would inhibit biochemical oxidation and in these cases, one must resort to a strictly chemical method.

By varying the experimental conditions under which a chemical oxygen consumed test is carried out, various values may be obtained. This is yet another reason why no correlation between the chemical and biochemical methods can be expected.

However, since a chemical method is often a valuable parameter in the study of polluting wastes, it is necessary to be familiar with the various methods now available for the determination of oxygen consumed.

Various oxidizing agents have been proposed for the determination of oxygen consumed. Of these only four have received any appreciable

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study, namely, potassium permanganate, potassium dichromate, ceric sulfate and iodic acid. Of these four, the first is still the recommended procedure in Standard Methods. However, that it is far from satisfactory is attested to by the amount of research work carried out in attempts to so modify it that the results would be more reproducible.

Ceric sulfate although a better oxidizing agent than potassium permanganate has not been used to any extent in the determination of oxygen consumed. It may be employed in the determination of glucose and has been found to be quite satisfactory for this purpose, its oxidizing power is greater than that of permanganate but is about 2/3 as effective as potassium dichromate.

Methods Commonly Used

Permanganate Method

As mentioned previously, potassium permanganate is still the standard oxidizing agent recommended by Standard Methods. Data will be presented later showing a comparison of this method with other methods available.

In the permanganate method the sample size is regulated so that at least 5 ml. of the 10 ml. of $KMnO_4$ is left after digestion. The sample is diluted to 100 ml. with distilled water if necessary. Ten ml. of standard $KMnO_4$ (containing 0.4 g of $KMnO_4$ per liter) plus 10 ml. of dilute, H_2SO_4 are added to the diluted sample and the mixture digested for 30 minutes in a boiling water bath. A blank is digested at the same time. Following the 30 minute period 10 ml. of standard oxalate are added and the excess titrated with standard $KMnO_4$. If strong sewage or industrial wastes are being examined a $KMnO_4$ solution 10 times the normal strength may be used.

$$\text{p.p.m. O.C.} = \frac{\text{net ml. of } KMnO_4 \times 100}{\text{ml. of sample}}$$

In Table 1 are given typical results obtained on a sample of industrial waste and o-cresol by the Standard permanganate procedure. It will be noted that the results are reproducible by this method. In the case of o-cresol only 65% of the theoretical oxygen consumed value can be obtained.

Dichromate Procedures

Adeney and Dawson(1) were among the first to use potassium dichromate in an acid solution for the oxidation of organic matter They heated the mixture at 100-110° C. for two hours and determined the excess dichromate by titrating with ferrous sulfate using an outside indicator.

The Adeney and Dawson method was modified at this Station so that a definite volume was heated at 100-110° C. for two hours. Ferrous ammonium sulfate was used to back titrate the excess dichromate and o-phenanthroline ferrous complex was used as an inside indicator.

Rhame(2) carried out the oxidation in a mixture of H_2SO_4 and H_3PO_4 to fumes. This procedure has been modified by Ingols(3) and will be discussed later. All of these procedures have one fault in common, namely, the oxidation is not carried out in a system which prevents the loss of volatile constituents in the waste, thereby, the true oxygen consumed value is not obtained.

At the present time this Station is undertaking a study of five different methods for the determination of oxygen consumed.

These methods are as follows:

Madison's Dichromate Method

Ingols' " "

U.S.P.H.S. " "

Iodic Acid Method

Potassium Permanganate (Standard Method).

A. Madison's Method.

Madison[4] has modified Rhame's method in some respects in order to increase the reproducibility of the results. However, the experience of this laboratory has been that of all of the methods proposed, Madison's method is subject to the widest variation in the oxygen consumed values obtained. The method is briefly as follows:

To the sample of waste in a 250 ml. Erlenmeyer flask is added 10 ml. of 0.05 N. $K_2Cr_2O_7$ and 20 ml. of H_2SO_4- H_3PO_4 mixture (1-1). If necessary, distilled water is added to bring the volume to 80 ml. The mixture is boiled until the volume is reduced to about 25 ml. The volume is then reduced until acid fumes just appear. Fuming is continued for four minutes without boiling. The acid mixture is cooled, diluted and the excess $K_2Cr_2O_7$ titrated with .025 N. ferrous ammonium sulfate using sodium diphenylamine sulfomate as an inside indicator.

$$\text{O.C. (p.p.m. } O_2) = \frac{(\text{ml. Blank} - \text{ml. for sample}) \times 200}{\text{Vol. sample}}$$

It should be pointed out that unless strict attention is paid to ascertaining the exact point of fuming and during the fuming period that wide variation in the results will be obtained. A typical series of results obtained by this method is given in Table 2, (second slide).

B. Ingols and Murray's Method.

Ingols and Murray further modified Rhame's procedure by refluxing the mixture for 60 minutes and determining the excess $K_2Cr_2O_7$ iodometrically. Their procedure is as follows:

Method

Reagents

1. Dichromate oxidizing reagent:
   1 vol. of conc. sulfuric acid C.P. 95%
   1 vol. of orthophosphoric acid C.P. 85%
   1.25 g. potassium dichromate per liter
   (Dissolve the dichromate in 20-25 ml. distilled water before adding acid)
2. Sodium iodide solution 20% C.P.
3. Sodium thiosulfate solution 0.025N standard
4. Soluble starch solution
5. Silver nitrate and potassium dichromate solutions for determining chlorides according to Standard Methods(5).

Apparatus

1. 250 ml. Erlenmeyer flasks with outer 24/40 Standard taper neck
2. Reflux Condenser with inner 24/40 Standard taper fitting

Procedure

Place 25 ml. of the oxidizing reagent in the 250 ml. flask with 10 ml. of sample. This mixture will boil at 145° C. under a reflux condenser. If raw sewage is used, approximately 5 ml. of sample will be needed, then 5 ml. of water must be added to provide a volume of 10 ml. of sample plus the 25 ml. of reagent. If a larger volume is

needed for dilute samples such as effluents and stream samples, then the excess water must be removed by evaporation until the temperature of the mixture reaches 145° C. (35.0 ml. total vol.).

Place the flask plus sample over a burner and reflux 60 minutes so that the fumes do not rise higher than one inch above the lowest cooling surface of the condenser. Cool; rinse down reflux condenser with approximately 100 ml. water; cool; add 3 ml. potassium iodide solution; wait 5 min.; then titrate the free iodine with the standard thiosulfate solution.

$$O.C. = \frac{\text{ml. for blank} - \text{ml. thio for sample} \times 200 - 0.23 \text{ p.p.m. } Cl^- \text{ ion}}{\text{ml. sample}}$$

In Table 3 are given typical results obtained by this method, (Slide 3). It is rather surprising that only 86% of the theoretical could be obtained in the oxidation of dextrose which is one of the most easily oxidized organic compounds studied. The reproducibility of results is seen to be quite good. However, the use of ferrous iron is to be preferred in the determination of the excess dichromate present over the iodometric procedure.

As with Rhame's procedure, Ingols and Murray tried to correlate O.C. values with those obtained biochemically. In Fig. 1 are shown comparisons for raw and settled sewage and trickling filter effluent. The O.D. values are multiplied by 0.68 on the assumption that the biochemical oxidation follows a k of 0. This has been shown to be an erroneous conclusion by this laboratory (5).

C. U.S.P.H.S. Method

As stated previously the method(6) used at this station is an adaptation of the Adeney and Dawson procedure. It has been found to

give reproducible results on a wide variety of organic compounds and some industrial wastes. The end-point is quite sharp and if over-titrated may be back titrated with the standard dichromate solution.

Recommended Procedure

Dilute an appropriate amount of sample to 50 ml. with distilled water in a 300 ml. round bottom flask with a taper joint neck. Add 25.0 ml. of 0.2500 N $K_2Cr_2O_7$ and 75 ml. of concentrated H_2SO_4 and reflux for 2 hours. For the best quantitative results, the 50% by volume of sulfuric acid is used. Cool and transfer the mixture to an Erlenmeyer flask and titrate the excess $K_2Cr_2O_7$ with approximately 0.2500 N ferrous ammonium, using ortho-phenanthroline ferrous complex as an indicator. A blank is refluxed at the same time, using the same amount of reagents and substituting 50 ml. of distilled water for the sample. The ferrous ammonium sulfate must be standardized daily.

Calculation:

$$O.C., \text{ p.p.m.} = \frac{(a-b) \times \text{Normality (Std. Fe)} \times 8000.}{\text{Vol. Sample}}$$

O.C. = Oxygen Consumed

a = ml. Fe $(NH_4)_2(SO_4)_2$ used for sample

b = ml. Fe $(NH_4)_2(SO_4)_2$ used for sample

Effect of Chlorides

In 1932 Bach (7) found that the oxygen consumed values of raw sewage were increased from 258 to 291 p.p.m. when the NaCl content varied from 20 to 2000 p.p.m. In Fig. 1 the effect of chlorides on oxygen consumed values obtained with N/4 $K_2Cr_2O_7$ is shown. When 50% by volume of H_2SO_4 is used, quantitative oxidation of chlorides is obtained over the range from 250 to 20,000 p.p.m. However, when 33%

by volume of H_2SO_4 is employed the results obtained are somewhat erratic, the amount of oxidation depending on the amount of N/4 $K_2Cr_2O_7$ used. With 50.0 ml. of the dichromate, the results are not as erratic as with 25.0 ml. The chloride correction in the latter instance is subject to a larger error.

As with most wet combustion methods employed, the method proposed has its limitations. However, the results obtained are reproducible and it is believed that the method will be useful in determining the approximate strength of sewage and industrial wastes. It is shown that hydrocarbons, as well as straight chain acids and alcohols, are scarcely attacked. In contrast to this, the aerobic bacteria are able to utilize and oxidize the latter two types of compounds as a food source. Branched chair aliphatic acids and alcohols are, as a rule, readily oxidized by the proposed chemical method, and there is no difficulty encountered in the oxidation of sugars. Phenolic compounds are also oxidized quantitatively. Chlorides are shown to be quantitatively oxidized at the higher acid concentration. Correction for the chloride content of industrial wastes may be made. With the lower acid concentration, however, the amount of oxidation is dependent upon the volume of N/4 $K_2Cr_2O_7$ used.

In the slide are given typical results obtained on various classes and types of organic compounds which may occur in wastes of either human or industrial origin.

Iodic Acid Method

In 1938 Dzyadzio[8] used KIO_3 in a 65 - 80% H_2SO_4 solution as the oxidizing agent and heated the mixture at 200° C. The excess iodate was determined iodometrically. He claims that the error obtained in

the oxidation of 14 organic compounds did not exceed 2 - 3% and that the method is superior to the dichromate method. Johnson, Tsuchiya and Halvorson[9] have also used the iodic acid method. In their work, they refluxed the mixture, if the sample was high in volatile acids, but with other samples, refluxing was not resorted to. It might be of interest to know that the industrial waste laboratory of the Standard Oil Company has adopted this method as their Standard procedure. It is also being recommended to the American Petroleum Institute for adoption.

I. Procedure for the Determination of Oxygen Demand of Wastes Low in Volatile Acids.

This method is recommended for wastes such as domestic wastes, creamery wastes and those wastes low in volatile acids.

A. Reagents:

(1) Standard KIO_3 solution (1.0 N). 35.67 grams of KIO_3 (C.P. or A.R. grade), which has been dried at 180° C. for 3 hours, is dissolved in distilled water and made up to 1 liter.

(2) Standard $Na_2S_2O_3$ solution, (ca.0.1 N) Approximately 25 grams of $Na_2S_2O_3 \cdot 5H_2O$ is dissolved in distilled water and made up to 1 liter. The solution may be preserved by the addition of 1 N NaOH added at the rate of 4 ml. per liter.

(3) Starch indicator-0.5% solution of soluble starch. This solution may be preserved by the addition of a pinch of HgI_2.

(4) Concentrated NaOH solution (50%)

(5) Standard HCl (ca.0.5.N) approximately 42 ml. of concentrated HCl is made up to 1 liter with distilled water. The exact strength may be determined by titration with Na_2CO_3.

(6) Standard NaOH solution (ca.0.5.N). Approximately 20 grams of NaOH is dissolved in distilled water and made up to 1 liter. The exact strength is determined by titration with the standard HCl solution.

(7) Indicator Solution-0.05% solution of Methyl or Brom Cresol Green.

B. Procedure:

(1) An appropriate amount of the waste sample to be analyzed is pipetted into a Kjeldahl flask (for most purposes a 300 ml. flask is satisfactory). The size of sample depends on the strength of waste. 5.0 ml. of the standard KIO_3 solution is carefully added. 3.0 ml. of concentrated H_2SO_4 is added. A small amount of ignited powdered pumice is added to prevent bumping.

(2) The flasks are then placed in a bath of Fisher bath wax. The temperature of the bath is raised to 190° C ± 5° and maintained there for 35 minutes after the contents of the flask have stopped boiling.

(3) The flasks are allowed to cool and the contents quantitatively transferred to a 500 ml. Erlenmeyer flask. Distilled water is used to wash out the contents of the Kjeldahl flask. We prefer to keep the total volume in the Erlenmeyer at about 200 ml.

(4) The free iodine formed during the iodate oxidation is removed by subjecting the contents of the Erlenmeyer flask to steam distillation until it is free of the color of iodine.

(5) 2 grams of KI are added to convert the residual iodate not required for the oxidation of organic matter to free iodine.

(6) The iodine is titrated with the standard $Na_2S_2O_3$ solution, adding a few drops of the starch indicator toward the end of the titration.

(7) After the thiosulfate titration the sample can be analyzed for ammonia nitrogen. (In the iodate oxidation reaction, any amino nitrogen in the sample will have been converted to ammonia.) The contents of the Erlenmeyer flask are made alkaline with concentrated NaOH solution and the flask immediately connected to the condenser of the ammonia still. The ammonia is distilled off into a flask containing a known volume of standard HCl containing a few drops of indicator. Approximately 150 ml. of distillate are collected.

(8) The excess acid is titrated with the standard NaOH solution.

(9) A control should be run simultaneously, using distilled water instead of a sample of waste.

II. Procedure for the Determination of Oxygen Demand of Waste High in Volatile Acids.

This method is recommended for wastes such as corn canning factory wastes and those wastes high in volatile acids.

A. Reagents:

Same as those used in Procedure for the Determination of Oxygen Demand of Wastes Low in Volatile Acids.

B. Procedure:

(1) A 5.0 ml. amount or aliquot of the waste sample to be analyzed is pipetted in a Kjeldahl flask (for most purposes a 300 ml. flask is satisfactory).

5.0 ml. of the standard KIO_3 solution is carefully added.

9.0 ml. of concentrated H_2SO_4 is added.

(2) The flasks are then attached to condensers and the flasks placed in a bath of Fisher bath wax (See B (2) under Procedure for the Determination of Oxygen Demand for Wastes low in Volatile acids for the method of preparation) for refluxing. The temperature of the bath is raised to 190° C ± 5° and maintained there for 1 hour.

(3) The flasks are allowed to cool. The contents are quantitatively transferred to a 2 liter Erlenmeyer flask. Distilled water is used to wash out the contents of the Kjeldahl flask and the total volume in the Erlenmeyer flask is kept at about 750 ml.

(4) The free iodine formed during the iodate oxidation is removed by subjecting the contents of the Erlenmeyer flask to steam distillation until it is free of the color of iodine. The volume of the flask contents is kept at about 750 ml. by heating the flask with a small auxiliary burner.

(5) The contents of the flask are allowed to cool. It is then quantitatively transferred to a 1 liter volumetric flask and made up to volume with distilled H_2O.

(6) A 500 ml. aliquot is then transferred to a 1 liter Erlenmeyer flask. 2 grams of KI are added to convert the residual iodate, not required for the oxidation of organic matter, to free iodine.

(7) The iodine is titrated with the standard $Na_2S_2O_3$ solution adding a few drops of the starch indicator towards the end of the titration.

(8) Kjeldahl determination for amino and ammonia N is made on a separate waste sample to determine the amounts of these substances simultaneously with the iodate oxidation.

(9) Controls should be run simultaneously for both the iodate oxidation and Kjeldahl determination, using distilled water instead of a sample of waste.

$$\text{p.p.m. O.C.} = \frac{6666}{\text{Vol. sample}} \times N_{\text{Thio}} \times \Delta V_{\text{Thio}}$$

ΔV = ml. for control - ml. for sample

The iodic acid method is the most tedious and time consuming of any of the methods given. The apparatus required is more involved and the titration of the excess KIO_3 iodometrically is much more cumbersome. The results compare favorably with those obtained with dichromate in most cases as shown in the slide.

Other Proposed Methods

Other methods have been proposed for the determination of oxygen consumed values based on the complete wet combustion of the organic

compounds contained in the waste. Among those may be mentioned the method of Mohlman and Edwards[10], who used chromic acid as the oxidizing agent and absorbed the liberated CO_2 in 0.1 N $Ba(OH)_2$. The excess $Ba(OH)_2$ was titrated with standard acid. This method as well as that of Burtle and Buswell[11] requires very careful manipulation and rather complicated apparatus. The method of Gilcreas[12] at present a tentative method in Standard Methods is also an example of complete wet combustion.

Comparison of Methods

In Table 4 are given typical results obtained on one sample of industrial wastes by the five different methods. It will be noted that Madison's method is subject to the widest variation and the results are quite low for a dichromate oxidation. The average obtained is not much higher than with the Standard permanganate method which is seen to give low but reproducible results. The results obtained with Ingols and the U.S.P.H.S. method compare quite favorably with the iodic acid showing a wider fluctuation and a lower oxygen consumed.

In Table 5 is given a statistical analysis of 100 determinations on an industrial waste sample with the five different methods. It will be noted that the range for Madison's method is almost twice the average value obtained. The U.S.P.H.S. method gives the lowest range as well as lowest standard deviation and coefficient of variation. The time required for the indicated number of replicates is the highest for the iodic acid method. It should be noted that of the 4.5 hours required for the U.S.P.H.S. method, 2 hours are required for the refluxing time. Work is being carried out now to try and reduce the length of the refluxing period.

Table 1

O. C. by Permanganate

p.p.m.

Replicates	Industrial Waste	O-Cresol
1	404	408
2	408	408
3	416	402
4	416	404
5	440	399
6	434	399
7	446	406
8	438	401
9	422	414
10	448	406
Av.		405
Theory		629
% of theory		65.

Table 2

O.C. by Madison's Method

p.p.m.

Replicates	Industrial Waste	O-Cresol	
1	653	475	396
2	914	480	374
3	610	491	368
4	823	505	377
5	560	478	363
6	440	480	432
7	594	484	396
8	525	503	389
9	536	476	400
10	701	475	437
Avg.		485	393
Theory		629	
% of Theory		77.	62.

Table 3

O.C. by Ingols-Murray Method

p.p.m.

Replicates	Industrial Waste	Dextrose
1	1141	209
2	1067	214
3	1097	206
4	1111	209
5	1115	204
6	1165	208
7	1167	208
8	1141	211
9	1129	201
10	1143	204
Avg.		208
Theory		237
% of Theory		86

Table 4

Comparison of Various Methods on Industrial Waste Sample

Replicates	Iodic Acid	Ingolls and Murray	Madison	Standard $KMnO_4$	U.S.P.H.S.
1	917	1148	435	470	1181
2	878	1174	544	493	1184
3	922	1144	405	483	1169
4	900	1076	515	476	1182
5	864	1092	307	461	1177
6	949	1100	453	417	1184
7	918	1140	741	476	1177
8	963	1134	749	438	1179
9	922	1142	776	442	1184
10	1005	852	461	453	1176

Table 5

Oxygen Consumed Determinations on National Aniline Divisions

Plant B & C Effluent

Method	Iodate	Ingols	Madison	Permanganate	U.S.P.H.S.
No. of Determ.	99	96	99	98	100
No. of Replicates	5	10	10	10	10
Mean	960	1153	690	463	1183
Range	223	591	1184	169	113
Sum of dev.^{2}	152325	514388	4,412,220	107495	24923
Variance	1554.3	5414.6	44,568	1108.2	251.7
Std. dev.	39.42	73.6	211.1	33.29	15.87
Confidence Lim. single det.	110	166.3	477	75.1	35.8
Confidence Lim. Mean	5.53	6.19	10.40	4.14	2.84
Coeff. of Variation	.0411	.0638	.3059	.0719	.0134
Time required for indicated No. of replicates, hours	7-3/4	3-3/4	7	3	4-1/2

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